

NITROGEN-CONTAINING ORGANOPOLYSILOXANES AND USE THEREOF

Patent Number: GB1409741

Publication date: 1975-10-15

Inventor(s):

Applicant(s):: ICI LTD

Requested

Patent: ☐ GB1409741

Application

Number: GB19720005494 19720207

Priority Number

(s): GB19720005494 19720207

IPC

Classification: C08G77/26 ; C08G77/54 ; C09G1/12

EC

Classification: C07F7/10, C08G77/388

Equivalents:

AU470310, AU5180573, ☐ BE795106, CA983947, ☐ DE2305988, ☐ FR2171158,
IT978858, ☐ JP49047499, ☐ NL7301640, ZA7300620

Abstract

Data supplied from the esp@cenet database - I2

BEST AVAILABLE COPY

PATENT SPECIFICATION

(11) 1 409 741

1 409 741

- (21) Application No. 5494/72 (22) Filed 7 Feb. 1972
 (23) Complete Specification filed 26 Jan. 1973
 (44) Complete Specification published 15 Oct. 1975 ✓
 (51) INT CL² C08G 77/26, 77/54/C09G 1/12
 (52) Index at-acceptance

C3T 1 6D11 6D1A 6D1B 6D2A 6D3 6D4A 6D4B 6D5 6D6
 6D8 6DX 6F2 6G7A 6G7D 6G7E 6G7F 6G7G
 6G7X 6H1 6H3 6H4D 6H4F 6H4G 6H4X 7B2 7D2
 7E1

C5W 5D 8A1 8A2 8A3 8B1 8B2 8B3

(72) Inventor JOHN HEATHCOTE ATHERTON



(54) NITROGEN-CONTAINING ORGANOPOLYSILOXANES AND USE THEREOF

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement—

This invention relates to new and useful nitrogen-containing organopolysiloxanes and to the use thereof.

A wide variety of nitrogen-containing compounds including nitrogen-containing organosilicon compounds are known and have been used for sundry purposes. Included among such compounds have been organopolysiloxanes having both alkoxy and γ -amino-propyl groups attached to the same or different silicon atoms.

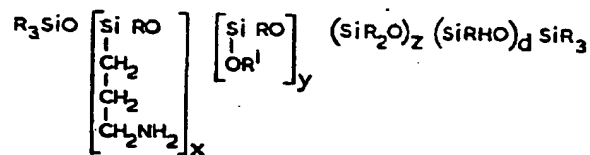
According to the present invention a new and useful class of organopolysiloxanes comprises organopolysiloxanes (A) having a proportion of nitrogen-containing groups of one or more of the formulae



with or without a proportion of groups of the formula $\text{NH}_2(\text{CH}_2)_3\text{Si}\langle$, the remaining silicon valences not attached to oxygen in the polysiloxane chain being occupied by monovalent substituted or unsubstituted hydrocarbon groups with or without a proportion of hydrogen.

Our invention also resides in a process for the production of organopolysiloxanes (B) having both γ -aminopropyl and OR' groups where R' is a monovalent hydrocarbon group, hydrogen, a monovalent hydrocarbon group substituted by NR_2^c groups, an oxyalkylene group of the general formula $(\text{C}_n\text{H}_{2n}\text{O})_c\text{R}''$ where n is 2 or 3 and c is an integer from 1 to 30 or a NR_2^c group where R'' is hydrogen or a monovalent hydrocarbon group.

These organopolysiloxanes (B) may be represented by the average general formula



wherein R is a monovalent substituted or unsubstituted hydrocarbon radical if desired, a proportion of the R groups being hydrogen, and is preferably a methyl group, R' is as hereinbefore defined, x is a number from 0.1 to 5, y is a number from 1 to 100, z is a number from 0 to 500 and d is a number from 0 to 49.

The nitrogen-containing organopolysiloxanes (A) of our invention may be

prepared by reacting allylamine with an organopolysiloxane containing a proportion of silicon-bonded hydrogen atoms, the reaction being carried out in presence of a catalyst of the kind known for use in the addition reaction between a compound containing silicon-bonded hydrogen and an unsaturated compound.

Organopolysiloxanes suitable for use in this reaction may be of the average general formula



wherein the group R is as hereinbefore defined, a is a number from 1 to 50, and z is as hereinbefore defined. Suitable groups R include, for example, methyl, phenyl and 3,3,3 trifluoropropyl groups. For many purposes it is preferred that the groups R be methyl groups. While a and z may vary as stated it is frequently preferred that a has a value from 1 to 10 and that z has a value from 0 to 100.

Suitable catalysts which may be used in the reaction include, for example, bis(diethylsulphide)platinous chloride, chloroplatinic acid, platinum chloride/olefin complexes such as cyclohexene platinous chloride and other forms of platinum catalyst containing combined platinum. It is normally preferred to use a catalyst which is soluble in the reaction mixture. The catalyst is normally used in an amount of from 10^{-2} to 10^{-7} moles per mole of SiH. It is, however, generally preferred to use from 10^{-3} to 10^{-4} moles per mole of SiH.

It is normally convenient to carry out the reaction by heating at, for example, from 30 to 200°C. At lower temperatures the speed of reaction is generally too slow for practical purposes. It is also preferable to carry out the reaction in presence of a solvent, for example, such as toluene, benzene or white spirits, and it is very often convenient to react at the reflux temperature of the reaction mixture.

It is also preferred to add the allylamine to the reaction mixture slowly and evenly. The relative proportions of allylamine and polysiloxane (C) which are reacted may vary widely depending on the product desired. The amount of allylamine may or may not be sufficient to react with all of the silicon-bonded hydrogen. It is, however, frequently preferred that the molar proportion of allylamine to silicon-bonded hydrogen should be 1:2 or thereabouts since it is not normally desired to react all the silicon-bonded hydrogen atoms.

The nitrogen-containing organopolysiloxanes (A) of our invention may be used for a variety of purposes such as, for example, treating materials such as silicas and cellulosic materials to render them hydrophobic. They attach to materials containing hydroxyl groups by silylation thereof giving Si—O—C bonds. They are, however, particularly useful as intermediates, especially for the preparation of organopolysiloxanes (B) containing both γ -aminopropyl and OR' groups.

A process of producing organopolysiloxanes (B) according to our invention comprises reacting certain nitrogen-containing organopolysiloxane (A) of our invention with a compound of the general formula R'OH where R' is as hereinbefore defined. In this process it is preferred that the nitrogen-containing organopolysiloxane (B) so produced should be free from silicon-bonded hydrogen. Compounds R'OH which may be used in this reaction include, for example, water, methanol, ethanol, propanol, butanol, isobutanol, benzyl alcohol, ethylene glycol, propylene glycol, ethanalamine, N,N-diethylethanalamine, N,N-diethylhydroxylamine and compounds of the general formula R'(OCH₂H_n)_cOH where R', n and c are as hereinbefore defined.

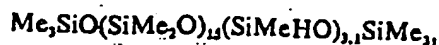
It is preferred to carry out the reaction between the poly-siloxane (A) and the hydroxyl containing compound in a solvent and this may be the same solvent as used in the preparation of polysiloxane (A). It is also generally preferred to react at the reflux temperature of the mixture. In many cases it is also found desirable to use a catalyst of the kind known for use in the reaction between compounds containing silicon-bonded hydrogen atoms and compounds containing hydroxyl groups. These include, for example, piperidine, diethylhydroxylamine, potassium hydroxide, and stannous octoate.

The polysiloxanes (B) are useful for a wide range of purposes including sizing agents for organic and glass fibres, emulsifying agents, waterproofing agents and other like applications. They are particularly useful for use as polish additives to confer detergent resistance thereon.

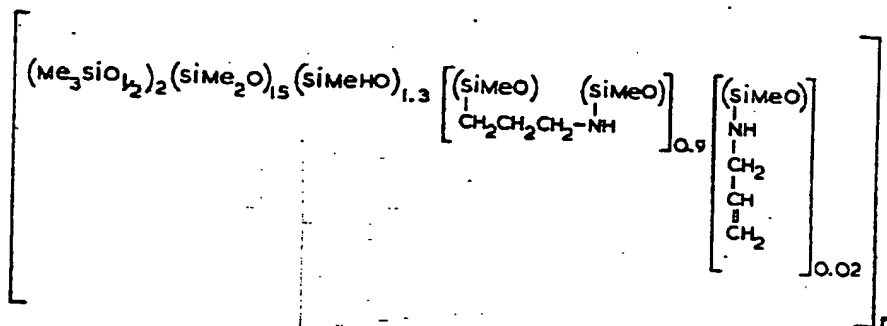
Our invention is further illustrated by the following examples in which all parts and percentages are by weight.

EXAMPLE 1.

1166.5 parts of a polysiloxane having the average formula

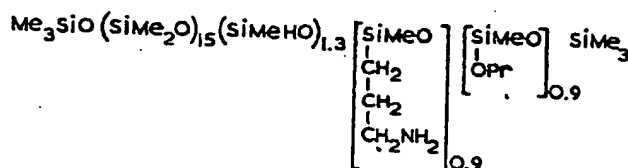


860 parts of toluene and 0.115 part of bis(diethylsulphide)platinous chloride were stirred and heated to reflux. 57 parts of allylamine were added dropwise to the refluxing solution over a period of 6 hours and heating under reflux continued for one hour after the addition was complete. Volatile materials were removed by distillation at 100°C under a pressure of 15 mm Hg to give 1220 parts of a pale orange-yellow oil having a viscosity of 53.7 centistokes at 25°C and a neutralisation equivalent of 1665. Quantitative infrared analysis showed that the product contained 42 per cent of the silicon-bonded hydrogen present at the start of the reaction. The product can be represented by the average formula



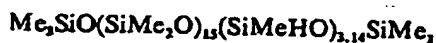
EXAMPLE 2.

41.25 parts of the product of Example 1, 21 parts of toluene and 8 parts of propanol were heated under reflux for 5 minutes (no gas was evolved) and the solution was devolatilised at 100°C under a pressure of 15 mm Hg to give a product having a neutralisation equivalent of 1760 and a viscosity of 31.2 cS at 25°C, represented by the average formula

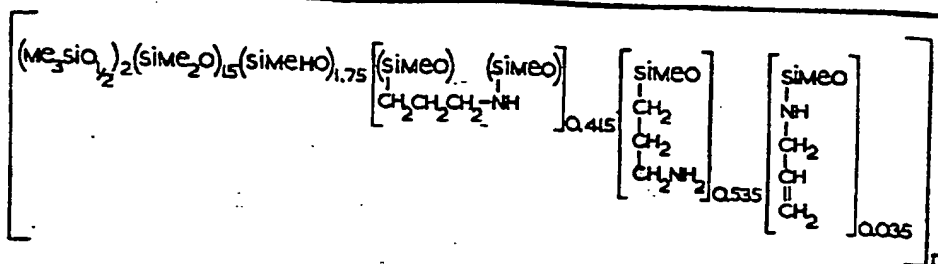


EXAMPLE 3.

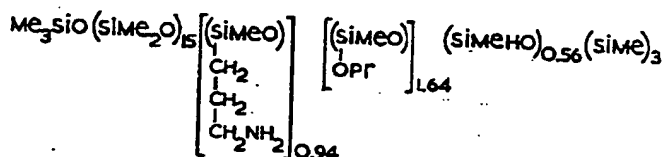
21.3 parts of a polysiloxane having the average formula



19.6 parts of toluene and 0.002 part of bis(diethylsulphide) platinous chloride were stirred and heated to reflux and 1.5 parts of allylamine added to the solution over a period of 2 hours. Infrared analysis showed that 44.5% of the available silicon-bonded hydrogen had been consumed at this stage. A sample was removed, and after devolatilisation at 100°C under pressure of 15 mm Hg was found to have a neutralisation equivalent of 1535. An additional sample was treated with its own volume of methanol, heated to reflux and again devolatilised under identical conditions to give a product having a neutralisation equivalent of 1613. This intermediate product can be represented by the average formula



4 parts of volatile materials were removed from the mixture by distillation at 100°C under a pressure of 15 mm Hg and a solution of 0.09 part of stannous octoate in 3.4 parts of propanol added dropwise to the refluxing solution. Heating under reflux was continued for two hours after the addition was complete after which the mixture was allowed to cool to 20°C and filtered. Solvent was removed by distillation at a temperature of 120°C and a pressure of 20 mm Hg to give 22 parts of an oil having a neutralisation equivalent of 1680 and represented by the average formula



Nitrogen analysis (Kjeldahl) 0.85%. Calc. 0.833%. Silicon-bonded hydrogen in product was measured by quantitative infra-red spectroscopy.

EXAMPLE 4.

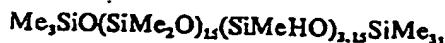
246 parts of a polysiloxane having the average formula



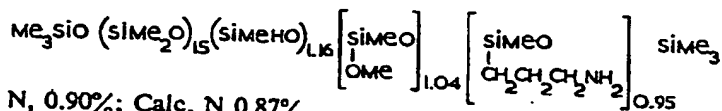
in 162 parts of toluene containing 0.020 part of bis(diethylsulphide) platinumous chloride was heated to reflux and 11.6 parts of allylamine added thereto at an even rate during 250 minutes. Thereafter a mixture of 23 parts of propanol and 12 parts of isobutanol containing 0.05 part of potassium hydroxide and 0.33 part of water was added during 35 minutes. Gas evolution ceased 90 minutes after the addition was complete and infra red spectroscopy showed the absence of silicon-bonded hydrogen from the reaction mixture. Volatile materials were removed by distillation at a pressure of 10 mm Hg and a temperature of 100°C to give 250 parts of an oil having a viscosity of 12.7 cS at 25°C and a neutralisation equivalent of 1460.

EXAMPLE 5.

878.5 parts of polysiloxane having the average formula



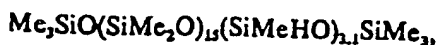
860 parts of toluene and 0.09 part of bis(diethylsulphide) platinumous chloride were heated to reflux and 53 parts of allylamine added dropwise over a period of 3 hours and the mixture thereafter heated under reflux for 3 hours. 770 parts of volatile materials were distilled off at atmospheric pressure. 1 part of stannous octoate, and 59 parts of methanol were added. The mixture was heated under reflux for 2 hours then devolatilised at 130°C and 80 mm Hg pressure to give 916 parts of an orange oil having a neutralisation equivalent of 1620 and a silanic hydrogen content of 0.075 per cent. It is represented by the average formula



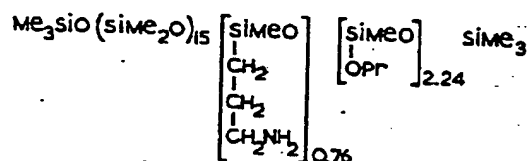
Found: N, 0.90%; Calc. N 0.87%

EXAMPLE 6.

467 parts of a polysiloxane having the average formula



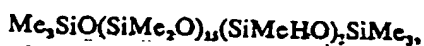
430 parts of toluene and 0.0445 part of bis(diethylsulphide)platinous chloride were heated to reflux and 21 parts of allylamine added dropwise over a period of 8 hours. 2 parts of diethylhydroxylamine and 58 parts of n-propanol were added to the mixture, which was then heated under reflux for a further 3 hours. Volatile materials were removed by distillation at 120°C and 55 mm Hg pressure. The product was a pale yellow oil having a neutralisation equivalent of 2160, and represented by the formula



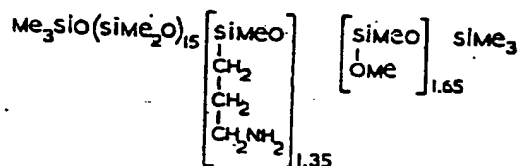
Infrared analysis of the product showed that no silicon-bonded hydrogen remained. 1.4 parts of hydrogen were evolved during the reaction (Theory for product shown: 1.46 parts).

EXAMPLE 7.

46.5 parts of polysiloxane having the average formula



129 parts of toluene and 0.1 part of bis-(diethylsulphide) platinous chloride were heated to reflux and 11.4 parts of allylamine added dropwise over a period of 2 hours. At the end of this time no silicon-bonded hydrogen could be detected in the product by infrared spectroscopy. Solvent was removed by distillation at 100°C and 15 mm Hg pressure to give a rubbery gell. This was dissolved in 100 parts of methanol, after which excess methanol was distilled off to give 45 parts of a dark mobile liquid having a neutralisation equivalent of 1030 and a methoxy content (as OMe) of 2.7%. It is represented by the formula



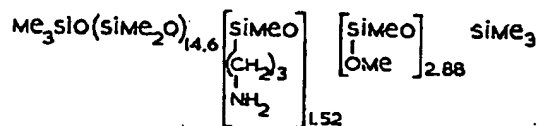
EXAMPLE 8.

348 parts of polysiloxane having the average formula



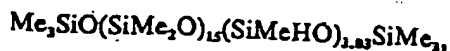
1290 parts of toluene and 0.8 part of bis(diethylsulphide)platinous chloride were heated to reflux and 53 parts of allylamine added dropwise over a period of 2 hours, after which time no silicon-bonded hydrogen could be detected in the product by infra-red spectroscopy.

The mixture was treated with 500 parts of methanol, heated under reflux for one hour and solvent removed by distillation at 190°C and 18 mm Hg pressure to give 363 parts of a dark brown oil having a neutralisation equivalent of 1100 and represented by the average formula

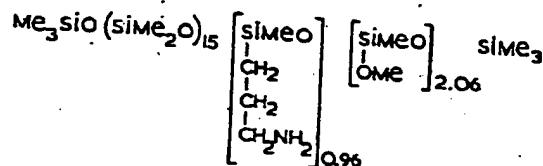


EXAMPLE 9.

480 parts of a polysiloxane having an average formula



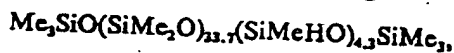
430 parts of toluene and 0.045 part of bis(diethylsulphide)platinous chloride were heated to reflux and 38 parts of allylamine added dropwise over a period of 3 hours. 2 parts of diethylhydroxylamine were added to the mixture, followed by 40 parts of methanol after which the mixture was heated under reflux for 5 hours. When hydrogen evolution ceased volatile materials were removed by distillation at 100°C and a pressure of 10 mm Hg to give 500 parts of a pale yellow oil of viscosity 37.3 cS at 25°C having a neutralisation equivalent of 1620 and represented by the average formula



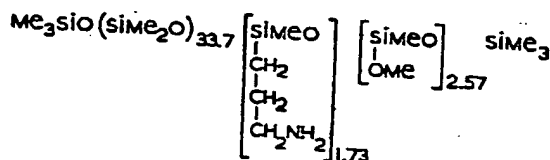
No silicon-bonded hydrogen could be detected in the product.

EXAMPLE 10.

A mixture of 676 parts of a polysiloxane having the average formula

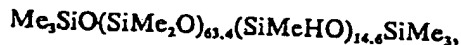


600 parts of toluene and 0.149 part of bis(diethylsulphide) platinous chloride were heated to reflux and allylamine added dropwise to the stirred mixture. When 38 parts of allylamine had been added the mixture gelled. The additional 16 parts of methanol were then added to the mixture which was heated to reflux for one hour after which solvent was removed by distillation at 100°C and 10 mm Hg to give 700 parts of a clear orange liquid having an equivalent weight of 1560 and represented by the average formula

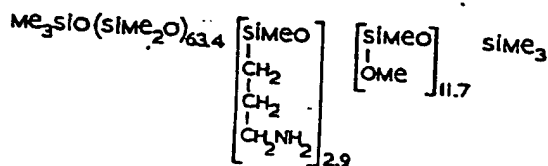


EXAMPLE 11.

A mixture of 46.5 parts of polysiloxane having the average formula

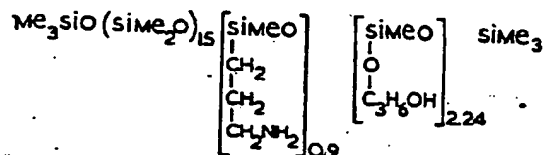


38 parts of toluene and 0.01 part of bis(diethylsulphide) platinous chloride was heated to reflux and allylamine added slowly to the refluxing mixture. When 1.5 parts of allylamine had been added the mixture gelled. 3 parts of methanol were added in order to dissolve the gell, followed by an additional 4.2 parts of allylamine. When gas evolution ceased a mixture of 1 part of diethylhydroxylamine in 16 parts of methanol was added. The mixture was heated again until gas evolution ceased and volatile materials were removed by distillation at 100°C/10 mm Hg to give 46 parts of a liquid having a neutralisation equivalent of 2130 and represented by the average formula



EXAMPLE 12.

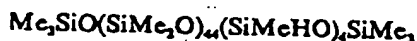
105 parts of the product of Example 1 and 82 parts of toluene were heated to reflux and a mixture of one part of stannous octoate, 8 parts of toluene and 15.2 parts of propylene glycol added thereto over a period of 5 minutes. The mixture was heated under reflux for two hours, during which time 0.173 part of hydrogen was evolved. (Theory: 0.182 part). The solution was filtered and devolatilised at 120°C and a pressure of 2 mm Hg to give 111.7 parts of a brown oil having a neutralisation equivalent of 1812 and represented by the formula



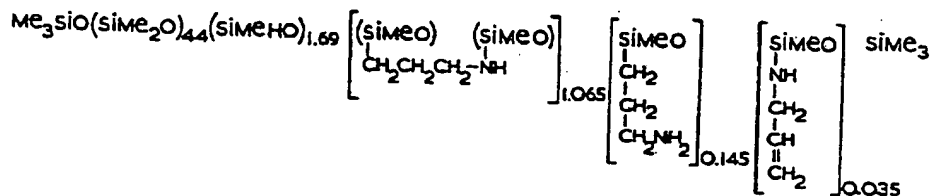
(Calc. neutralisation equivalent: 1823).

EXAMPLE 13.

A mixture of 1200 parts of a polysiloxane having the average formula

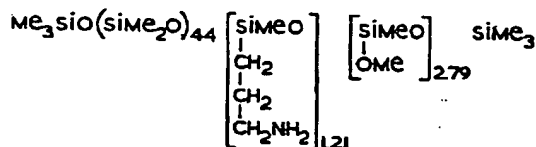


and a viscosity of 51 cS at 25°C, 690 parts of toluene and 0.1 part of bis (diethylsulphide)platinous chloride was heated to reflux and 30.2 parts of allylamine were added dropwise over a period of 2 hours. Volatile materials were removed by distillation at 120°C and 2 mm Hg pressure to give 1211 parts of a polysiloxane having a neutralisation equivalent of 3000 and a viscosity of 304 cS at 25°C. Quantitative infrared analysis showed that the product contained 42.2 per cent of the silicon-bonded hydrogen present at the start of the reaction. The product can be represented by the average formula



EXAMPLE 14.

330 parts of the product of Example 13 and 170 parts of toluene was heated to reflux and a mixture of 2 parts of diethylhydroxylamine and 44 parts of methanol added to these over a period of 30 minutes. Heating under reflux was continued for 6 hours after the addition was complete, by which time hydrogen evolution had ceased. A total of 0.28 part of hydrogen was evolved. (Theory: 0.306 part). The product was isolated by distillation at 130°C and 15 mm Hg pressure to give 336 parts of an oil having a neutralisation equivalent of 3140, and represented by the average formula



EXAMPLE 15.

Ten liquid, non-abrasive solvent dispersion polishes were prepared by stirring for 10 minutes at 85°C and then allowing to cool, a mixture of 94.9 parts of mineral spirit, 2.0 parts of the product of one of Examples 5 to 12 and 14, 0.5 part of a trimethylsilyl-ended poly(dimethylsiloxane) of viscosity 300 cS at 25°C, 0.2 part of

tan soft micro-crystalline wax, 0.1 part of filtered Carnauba wax and 2.3 parts of a synthetic Montan wax.

Each polish was found to impart a detergent resistant finish to a black nitro-cellulose-lacquered panel. The polish films were unimpaired by twenty washes with a 1 per cent solution of a commercially available car-wash detergent.

EXAMPLE 16.

Three water based emulsion car polishes were prepared by heating to 85°C in separate vessels mixtures of

A) 1.2 parts of a trimethylsilyl-ended poly(dimethylsiloxane) of viscosity of 300 cS at 25°C, 3.0 parts of the product of Examples 5, 8 and 14, 2.8 parts of yellow No. 1 Carnauba wax 6.6 parts of Paraffin wax having a melting point of 130—135°F, 2.0 parts of oleic acid and 27.8 parts of mineral spirit, and

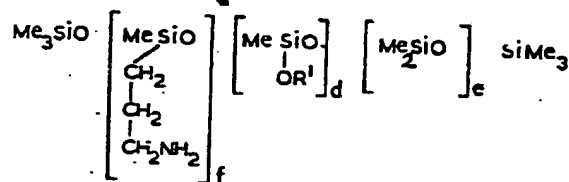
B) 1.4 parts of morpholine, 46.2 parts of water and 10.0 parts of a hydrophilic aluminium silicate; adding (B) slowly to (A) with continuous stirring, allowing the resulting mixtures to cool to 65°C and thereafter adding 5 parts of a 1 per cent aqueous solution of "Viscofas" (Registered Trade Mark) X100,000 with good stirring. The mixtures were stirred well for 5 minutes, homogenised and allowed to cool to 25°C to give liquid emulsion polishes.

All three polishes showed immediate resistance to washing with detergent solutions. The polish films were unimpaired by twenty washes with a 1 per cent solution of a commercially available car-wash detergent.

EXAMPLE 17.

Three oil-based emulsion car polishes were prepared by heating separately to 85°C mixtures of (A) 1.5 parts of a trimethylsilyl-ended poly(dimethylsiloxane) having a viscosity of 100 cS at 25°C, 3.0 parts of the product of Examples 5, 8 and 14, 3.0 parts of Yellow No. 1 Carnauba wax, 2.0 parts of a microcrystalline wax, 1.3 parts of a cationic emulsifying agent, 10 parts of an oleophilic aluminium silicate, 1.7 parts of an oxidised castor oil and 36 parts of mineral spirit, and (B) 41.4 parts of water containing 0.1 part of sodium nitrite; adding (B) to (A) with stirring, cooling to 60°C and homogenising. Thereafter the mixtures were allowed to cool slowly to 40°C and packed into chilled containers to give paste emulsion polishes. All three polishes showed immediate resistance to washing with detergent solutions.

In our application No. 598/75 (Serial No. 1,409,742), which is divided out of this application, there is claimed nitrogen-containing organopolysiloxanes of the average general formula



where R' is a monovalent hydrocarbon group, hydrogen, a monovalent hydrocarbon group substituted by NR²₁ groups, an oxyalkylene group of the general formula (C_nH_{2n+1}O)_nR² where n is 2 or 3 and c is an integer from 1 to 30 or a NR²₁ groups where R² is hydrogen or a monovalent hydrocarbon group, f is a number from 0.1 to 5.0, d is a number from 1 to 4.99 and e is a number from 0 to 500. There is also claimed a process for producing such organopolysiloxanes comprising reacting allylamine with an organopolysiloxane of average general formula



where a is a number from 1.1 to 9.9 and e is a number from 0 to 500 in the presence of a catalyst and thereafter reacting the reaction product with a compound of the general formula R'OH.

WHAT WE CLAIM IS:—

1. Organopolysiloxanes (A) having a proportion of nitrogen-containing groups of one or more of the formulae



5 with or without a proportion of groups of the formula



the remaining silicon valences not attached to oxygen in the polysiloxane chain being occupied by monovalent substituted or unsubstituted hydrocarbon groups with or without a proportion of hydrogen.

10 2. Organopolysiloxanes according to Claim 1 wherein the remaining silicon valences are occupied by groups selected from methyl, phenyl and 3,3,3-trifluoropropyl groups and hydrogen.

15 3. Organopolysiloxanes as claimed in Claim 1 substantially as hereinbefore described and with particular reference to the foregoing examples 1, 3 to 11 and 13.

4. A process for the production of organopolysiloxanes as claimed in any of Claims 1 to 3 comprising reacting allylamine with an organopolysiloxane containing a proportion of silicon-bonded hydrogen atoms in the presence of a catalyst.

20 5. A process according to Claim 4 wherein the organopolysiloxane containing silicon-bonded hydrogen atoms is of the average general formula:



wherein the group R is a monovalent substituted or unsubstituted hydrocarbon group, a is a number from 1 to 50, and z is a number from 0 to 500.

25 6. A process according to Claim 5 wherein a has a value from 1 to 10 and z has a value from 0 to 100.

7. A process according to either of Claims 5 or 6 wherein the catalyst is used in an amount of from 10^{-3} to 10^{-2} moles per mole of SiH .

30 8. A process according to any of Claims 4 to 7 wherein the reaction is carried out by heating at from 30 to 200°C.

9. A process according to Claim 8 wherein a solvent is used and reaction is effected by heating at the reflux temperature of the reaction mixture.

35 10. A process according to any of Claims 4 to 9 wherein the molar proportions of allylamine to silicon-bonded hydrogen is about 1:2.

11. A process for the production of organopolysiloxanes as claimed in any of Claims 1 to 3 substantially as hereinbefore described and with particular references to the foregoing examples 1, 3 to 11 and 13.

40 12. A process for the production of organopolysiloxanes (B) having both γ -aminopropyl and OR' groups where R' is a monovalent hydrocarbon group, hydrogen, a monovalent hydrocarbon group substituted by NR'_2 groups, an oxyalkylene group of the general formula $(\text{C}_n\text{H}_{2n}\text{O})_c\text{R}''$ where n is 2 or 3 and c is an integer from 1 to 30 or a NR'_2 group where R'' is hydrogen or a monovalent hydrocarbon group comprising reacting certain nitrogen-containing organopolysiloxanes (A) as claimed in any of Claims 1 to 3 with a compound of the general formula $\text{R}'\text{OH}$.

45 13. A process according to Claim 12 wherein the product is free from silicon-bonded hydrogen.

50 14. A process according to either of Claims 12 or 13 wherein the compound $\text{R}'\text{OH}$ is methanol, ethanol, propanol, butanol, isobutanol, benzyl alcohol, ethylene glycol, propylene glycol, ethanolamine, N,N -diethylethanolamine, N,N -diethylhydroxylamine or a compound of the general formula $\text{R}''(\text{OC}_n\text{H}_{2n})_c\text{OH}$ where n , c and c are as defined in claim 12.

55 15. A process according to any of Claims 12 to 14 wherein the reaction is carried out in presence of a catalyst selected from piperidine, diethylhydroxylamine, potassium hydroxide and stannous octoate.

16. A process for the production of organopolysiloxanes according to Claim 12 substantially as hereinbefore described and with particular reference to the foregoing examples 2, 3, 5 to 12 and 14.

17. Polish compositions containing a proportion of an organopolysiloxane produced by a process claimed in any one of Claims 12 to 16.
18. Polish compositions substantially as hereinbefore described and with particular reference to the foregoing examples 15 to 17.

J. L. BETON,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1975.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.